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NRL Report 4885

THE SILVER OXIDE-ZINC ALKALINE PRIMARY CELL

PART IV - ANODIC CHARACTERISTICS OF ZINC ALLOYS

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FC

February 8, 1957



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ABSTRACT

Preliminary work has been done on determining the capacity of the silver oxide-zinc alkaline cell when using various zinc alloys as a sheet anode. Most alloying elements decrease cell capacity, particularly if they are present in appreciable amounts. Mercury definitely improves cell capacity. A few other elements such as cobalt and calcium show some increased cell capacity but need further testing.

The grain structure of electrodes made of zinc and its alloys has a large effect on cell capacity.

Most of the zinc alloys were found to roll better at very high temperatures.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE SILVER OXIDE-ZINC ALKALINE PRIMARY CELL

Part IV - Anodic Characteristics of Zinc Alloys

BACKGROUND

Much of the demand for the silver oxide-zinc alkaline battery is based on two factors: the high capacity in watt-hours per unit weight of cell and the high current density at which this power can be produced. Any improvement in either of these factors would be highly desirable.

During cell discharge silver oxide is reduced at the positive plate and zinc is oxidized at the negative plate. The electrolyte is a solution of potassium hydroxide. As long as sufficient silver oxide and electrolyte are present, cell failure will nearly always occur at the zinc electrode; therefore, any improvements made in the existing cell will have to be made by improving the zinc plate.

During cell discharge, zinc oxidizes and may go either partially or completely into solution in the electrolyte. Films of varying physical properties can be observed on the zinc electrode during various discharge conditions. Cell failure is generally marked by a fairly rapid drop in the potential of the zinc, which indicates the formation of a nonporous film as a possible cause of failure. Elements which alloy with zinc and change its crystalline structure and other physical properties would be expected, for this reason as well as others, to affect cell capacity. Such effects might be either positive or negative. It is desirable to know if any elements will increase capacity, and also to know if any will decrease capacity so that they may be avoided.

A study has been made of the cell capacities of electrodes made from various zinc alloys. This investigation is incomplete, more data is needed, and the results should be used only as a basis for further study.

EXPERIMENTAL METHODS

Alloys were prepared by melting together with stirring weighed amounts of zinc and the alloying elements under an atmosphere of nitrogen. The melt was rapidly cooled, and the resultant 1-inch cylinder rolled out into a sheet approximately 0.020 inch thick. The sheet was cut into electrodes 1-1/2 inches square. One negative and two positive electrodes, separated by polystyrene spacers, were assembled in a tight fitting polystyrene case and enough electrolyte added to barely cover the plates. Thus, the volume of electrolyte varied with each assembly. The effective area of both sides of the negative plate was 4.26 square inches. All discharge currents and electrolyte volumes in this report refer to this size cell and would have to be divided by 4.26 square inches to obtain the current densities in amperes per square inch and the electrolyte volumes per square inch.

The zinc alloys were not subjected to chemical analysis. It was assumed that each alloy was homogeneous, and its composition was calculated from the weight of the original constituents.

In most cases three zinc alloys were prepared from the element being tested. The lowest concentration of the alloying element was approximately 0.05 percent, the intermediate concentration was approximately 0.5 percent, and the highest concentration varied from 2 to 5 percent depending on the alloy diagram, with aluminum concentrations being as high as 50 percent. These three alloys were prepared from each of the following elements: tin, bismuth, antimony, cadmium, mercury, lead, magnesium, copper, aluminum, cobalt, nickel, manganese, selenium, tellurium, lithium, silver, chromium, iron, potassium, and sodium. Approximately 0.05 and 0.5 percent alloys were prepared from each of these elements: calcium, strontium, barium, indium, arsenic, thallium, titanium, tungsten, boron, silicon, and vanadium. A few of these alloys were not tested because they were so brittle that no way was found to roll them into a sheet of satisfactory thickness.

METALLOGRAPHY

The grain structure of zinc and its alloys was found to be of considerable importance, not only because of the difficulties encountered in the mechanical rolling of most zinc alloys, but also because of the appreciable variation in cell capacity obtained by changing the grain structure of the specific zinc alloy being used as the anode.

The zinc lattice is of the hexagonal close-packed type and the fundamental crystal unit may be considered to be a hexagonal prism. The height of this unit cell is 4.9349 Å. The length of a side of the base of this unit cell is 2.6589 Å, which is the shortest distance between atoms in the basal plane (0001).

If a stress exceeding the elastic limit is applied to a crystal unit, consideration must be given to the stresses along the basal plane (0001) and the pyramid face ($10\bar{1}2$).

In metals the slip plane is the plane of highest atomic density, wherein the atoms are closest and are united with the greatest cohesive force. Such planes are separated from each other by the greatest interatomic distance. As would be expected, the slip plane in zinc is the basal plane. Slip occurs in the direction of that one of the three hexagonal axes, lying in the basal plane, which most nearly coincides with the direction of maximal shear. There also may be a small amount of tilting or rotation of the basal planes as they attempt to align themselves parallel to the direction of stress. A single crystal of zinc will stretch under plastic deformation into a thin ribbon having an elliptical cross section, whose major axis is approximately the same as the initial diameter of the crystal. Slip may also occur along this major axis. Even though slip occurs easily and if continued can result in extensive deformation, the simple geometric arrangement of the atoms in the zinc crystal will not be greatly disturbed.

A slightly higher stress than that necessary to cause a basal slip will, if applied in the proper direction, cause twinning to occur along the pyramid face ($10\bar{1}2$) (1). Twinning does not cause much deformation, the maximum reduction in thickness perpendicular to the basal plane being 6.75 percent (2). Twinning produces a reoriented space lattice in the twinned layers in which the basal plane is at an angle of $94^{\circ}5'$ to the pre-existing basal plane and lies approximately in one of the six prism face positions, depending on the pyramid face on which twinning has occurred. This is very important, in that a continued application of the original stress will then cause further slip on the new basal plane.

The practical result is that, when zinc is rolled, twinning occurs in such a manner that the basal planes of the resulting crystals will be in a position favorable to basal slip in the

direction of rolling. Therefore the crystals of rolled zinc will tend to be uniformly oriented (1). As a result of stresses set up in cooling, cast zinc will often show considerable twinning.

Upon heating cold-worked zinc, recrystallization will occur slightly above room temperature. Evidence of the twinning will disappear and a very uniform structure will result. Annealed strip zinc will have some crystalline orientation. The annealing incident to hot rolling is not sufficient to remove all the evidence of twinning.

Selective grain growth may occur in zinc under certain conditions, such as a strain gradient. This effect may occur at a temperature below that at which complete crystallization ordinarily occurs. The effect is so great in heating a slightly strained piece of zinc to the recrystallization temperature that it is difficult to pass rapidly enough through the temperature range at which selective grain growth occurs to prevent a deleterious coarsening of the grain structure.

Strain hardening by cold rolling is done by using very light reductions on cooled rolls. Strain hardening is affected by alloying elements in solid solution, cadmium in particular showing a large increase in this property. Cadmium has a strengthening and hardening effect on zinc but less than 0.2 percent will not affect the working properties of zinc.

Iron forms a compound with zinc which is hard and brittle and whose melting point is higher than that of zinc; hence, it appears as primary crystallites which embrittle the alloy and interfere seriously in its working. Manganese and nickel have a similar effect (1).

Tin and zinc form a very brittle eutectic which forms thin, almost continuous films along the grain boundaries. As little as 0.005 percent tin will make zinc too brittle to roll (1, 3). The presence of up to 1.5 percent lead does not seriously interfere in the rolling of zinc (3). Magnesium forms a compound $MgZn_2$, which is very hard and brittle and which forms an eutectic with zinc which is also very brittle (1).

DATA AND DISCUSSION OF RESULTS

Rolling

There was no information available on the rolling properties of most of the alloys that were prepared. Attempts to cold roll them and to roll them at moderately elevated temperatures were highly unsuccessful. Most of the alloys would crumble or on successive passes through the rolls would crack to such an extent that a satisfactory sheet could not be obtained. The fewest failures and the best results were obtained by rolling at very high temperatures.

The best results obtained are given in Table 1. The composition is based on the analysis of the homogeneous alloy that would be formed from the weights of the metals used in its preparation. The probable crystal structure of the alloy is that given in the literature; (M_1, M_2) designates a saturated solution of metal M_1 in metal M_2 . In the last column, "Badly cracked" means the alloy cracked so bad on that pass that it could not be rolled any further without breaking and had to be discarded. The condition of the edges of the final 0.020-inch-thick rolled sheet is given wherever it was not perfect. Thus, "Badly cracked sheet" means the edges of the final rolled sheet were badly cracked but could be trimmed off and the sheet used.

TABLE 1
Rolling Properties of Zinc Alloys

Composition	Rolling Temperature (°C)	Structure	Results of Rolling
0.050% Aluminum	357	(Al, Zn) + (Zn, Al)	Rolled easily
0.50% Aluminum	357	(Al, Zn) + (Zn, Al)	Rolled easily
4.89% Aluminum	357	(Al, Zn) + (Zn, Al)	Rolled easily
9.05% Aluminum	438	(Al, Zn) + (Zn, Al)	Cracked on ends, trimmed and rolled; slightly cracked sheet
50% Aluminum	438	(Al, Zn) + (Zn, Al)	Badly cracked on 4th pass
0.050% Antimony	343	Zn + Zn ₃ Sb ₂	Broke on 1st pass
0.51% Antimony	288	Zn + Zn ₃ Sb ₂	Rolled easily
4.73% Antimony	371	Zn + Zn ₃ Sb ₂	Rolled easily
0.050% Arsenic	357	Zn + β Zn ₃ As ₂	Rolled easily
0.49% Arsenic	357	Zn + β Zn ₃ As ₂	Rolled easily
0.049% Barium	357	—	Rolled easily; slightly cracked sheet
0.48% Barium	357	—	Rolled easily
0.050% Bismuth	343	Zn + (Zn, Bi)	Broke on 1st pass
0.50% Bismuth	343	Zn + (Zn, Bi)	Broke on 2nd pass
4.76% Bismuth	343	Zn + (Zn, Bi)	Broke on 1st pass
0.048% Boron	357	—	Rolled easily
0.20% Boron	357	—	Rolled easily
0.054% Cadmium	371	(Cd, Zn)	Rolled easily
0.49% Cadmium	371	(Cd, Zn)	Broke apart
5.05% Cadmium	288	(Cd, Zn) + (Zn, Cd)	Crumbled
0.047% Calcium	357	Zn + Ca Zn ₁₀	Badly cracked
0.49% Calcium	357	Zn + Ca Zn ₁₀	Rolled fair, badly cracked sheet
0.048% Chromium	357	—	Badly cracked on 1st pass
0.49% Chromium	357	—	Rolled fair
0.031% Cobalt	357	(Co, Zn) + (Zn, CoZn ₄)	Rolled easily
0.049% Cobalt	357	(Co, Zn) + (Zn, CoZn ₄)	Rolled easily
0.10% Cobalt	357	(Co, Zn) + (Zn, CoZn ₄)	Rolled easily
0.49% Cobalt	385	(Co, Zn) + (Zn, CoZn ₄)	Badly cracked
2.98% Cobalt	438	(Co, Zn) + (Zn, CoZn ₄)	No good
0.050% Cobalt	357		Rolled fair to 1/8 inch, then cracked on sides, but finished satisfactorily
0.195% Mercury			

TABLE 1 (Cont'd.)

Composition	Rolling Temperature (°C)	Structure	Results of Rolling
0.050% Copper	357	η Brass	Rolled easily
0.50% Copper	357	η Brass	Rolled easily
4.9% Copper	438	$\epsilon + \eta$ brass	Work-hardened rapidly and cracked — no good
0.049% Indium	357	—	Broke
0.49% Indium	357	—	Crumbled on 1st pass
0.053% Iron	357	(Fe,Zn) + (Zn,FeZn ₇)	Rolled fair — cracked on end
0.50% Iron	357	(Fe,Zn) + (Zn,FeZn ₇)	Rolled fair — cracked on edges; slightly cracked sheet
0.051% Lead	274	Zn + Pb	Rolled easily
0.50% Lead	316	Zn + Pb	Rolled easily
4.76% Lead	260	Zn + Pb	Badly cracked on 1st pass
0.050% Lithium	357	—	Rolled fair with cracking on edges; end cracked at 0.5 inch — trimmed
0.51% Lithium	357	—	Rolled fair, work hardened fast
0.025% Magnesium	357	(Mg,Zn) + MgZn ₅	Rolled all right but work hardened
0.53% Magnesium	357	(Mg,Zn) + MgZn ₅	Cracked on ends, trimmed and finished rolling, badly cracked sheet
3.4% Magnesium	357	(Mg,Zn) + MgZn ₅	Broke on 1st pass
0.050% Manganese	357	(Mn,Zn)	Rolled easily
0.31% Manganese	357	(Mn,Zn) + MnZn ₇	Rolled fair, work hardened some
0.50% Manganese	357	(Mn,Zn) + MnZn ₇	Rolled easily
0.050% Mercury	316	Zn + Hg	Rolled fair
0.21% Mercury	357	Zn + Hg	Rolled easily
0.51% Mercury	316	Zn + Hg	Rolled fair, slight tendency to crack
0.99% Mercury	274	Zn + Hg	Rolled fair, slight tendency to crack
1.56% Mercury	274	Zn + Hg	Started to crack
1.56% Mercury	316	Zn + Hg	Rolled fair, badly cracked sheet
4.76% Mercury	316	Zn + Hg	Broke on 1st pass
4.76% Mercury	371	Zn + Hg	Broke on 2nd and 3rd pass

TABLE 1 (Cont'd.)

Composition	Rolling Temperature (°C)	Structure	Results of Rolling
0.051% Nickel	357	(Ni,Zn) + (Zn,Ni Zn ₃)	Rolled easily
0.50% Nickel	385	(Ni,Zn) + (Zn,Ni Zn ₃)	Rolled fair
2.93% Nickel	438	(Ni,Zn) + (Zn,Ni Zn ₃)	Work hardened and badly cracked — no good
0.053% Potassium	357	Zn + K _x Zn _y	Rolled fair — cracked on edges, badly cracked sheet
0.50% Potassium	357	Zn + K _x Zn _y	Rolled fair — cracked on edges, slightly cracked sheet
0.049% Selenium	177	Zn + Se	Rolled easily
0.49% Selenium	177	Zn + Se	Rolled easily
3.44% Selenium	177	Zn + Se	Rolled easily
0.052% Silicon	357	—	Rolled easily
0.048% Silver	357	(Ag, Zn)	Rolled easily
0.50% Silver	357	(Ag, Zn)	Rolled easily
4.74% Silver	357	(Ag,Zn) + (hex. 60.5 - 78.1% Zn)	Rolled easily
0.048% Sodium	357	Zn + Zn _x Na _y	Rolled easily, slightly cracked sheet
0.49% Sodium	357	Zn + Zn _x Na _y	Cracked badly, rolled a portion into a very badly cracked sheet 0.05-inch thick
0.050% Strontium	357	—	Rolled easily
0.45% Strontium	357	—	Rolled easily
0.053% Tellurium	357	Zn Te + Zn	Rolled easily
0.50% Tellurium	385	Zn Te + Zn	Rolled easily
3.61% Tellurium	438	Zn Te + Zn	Rolled easily
0.049% Thallium	357	Zn + Tl	Rolled easily
0.52% Thallium	357	Zn + Tl	Broke on 2nd pass
0.05% Tin	371	Zn + (Zn,Sn)	Broke on 2nd pass
0.49% Tin	371	Zn + (Zn,Sn)	Broke on 2nd pass
4.76% Tin	371	Zn + (Zn,Sn)	Broke on 2nd pass
0.054% Titanium	357	—	Rolled easily
0.49% Titanium	357	—	Rolled easily with slight cracking, very slightly cracked sheet

TABLE 1 (Cont'd.)

Composition	Rolling Temperature (°C)	Structure	Results of Rolling
0.049% Tungsten	357	—	Rolled easily with some cracking on last 2 passes, very slightly cracked sheet
0.50% Tungsten	357	—	Rolled easily
0.055% Vanadium	357	—	Rolled easily
99.999% Zinc	357	Zn	Rolled easily

Standards

Discharges of cells of the various zinc alloys were made at that concentration of electrolyte which gave maximum cell capacity using a pure zinc sheet negative electrode of 4.26 square inches area at the particular discharge conditions. Three discharge conditions were used

2 amperes, 20°C, 35% KOH,

3 amperes, 20°C, 33% KOH,

0.6 amperes, -20°C, 33% KOH.

For the first two cases, the most effective concentrations of electrolyte were already known (4). In the third case, it was determined in the following manner: A number of measurements of the cell capacity using pure zinc electrodes were made at 0.6 ampere and -20°C for several concentrations of electrolyte. Since the cell capacity at a given set of conditions is known to be directly proportional to the volume of electrolyte, these data may be plotted as a straight line going through the origin (4). The average capacity for various amounts of electrolyte is the least square solution for a line passing through the origin and having the square of the standard error of y , the cell capacity, directly proportional to x , the electrolyte volume. This is shown for 33% KOH in Fig. 1.

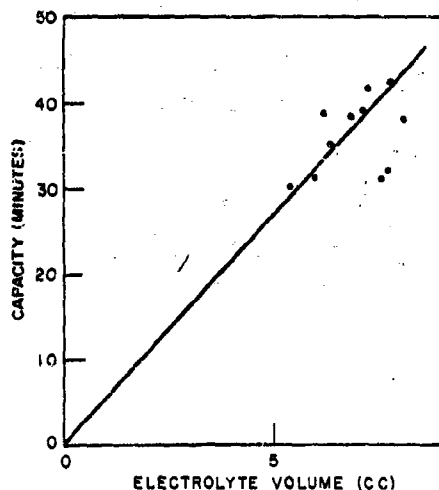


Fig. 1 - Cell capacity of pure zinc electrodes using 33% KOH at 0.6 ampere and -20°C

The slope (b) of such lines is found from the equation

$$b = \frac{\sum y}{\sum x} \quad (1)$$

Electrolyte concentrations from 32 to 36 percent were investigated and the slopes determined. The results are shown in Table 2. These values are plotted in Fig. 2 and show that 33% KOH is the most effective concentration of electrolyte for use with pure zinc electrodes at 0.6 ampere and -20°C .

Similar standards had been determined for pure commercial zinc sheet electrodes discharged at 2 amperes, 20°C , 35% KOH and at 3 amperes, 20°C , 33% KOH (4). The standard straight lines showing the relationship of cell capacity to electrolyte volume at these discharge conditions are plotted in Fig. 3 where they are labeled A. An attempt was made to duplicate these earlier data and the results are plotted as lines B of Fig. 3. A very definite difference was obtained.

TABLE 2
Ratio of Cell Capacity to
Electrolyte Volume at 0.6
Ampere and -20°C

Electrolyte Concentration (%)	Slope (min/cc)
32	5.0
33	5.38
34	5.0
35	4.36
36	3.82

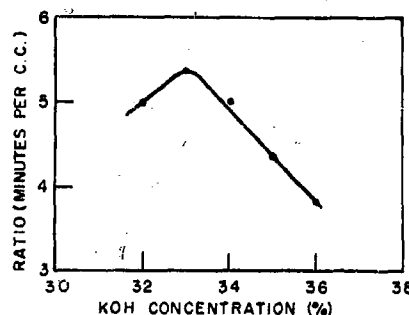


Fig. 2 - Ratio of cell capacity to electrolyte volume for various concentrations of electrolyte at -20°C and 0.6 ampere current

Samples of pure zinc were melted, cast, and rolled into sheets in the same way that the alloys were prepared. These were discharged in cells and the results are plotted as lines C of Fig. 3. Pure zinc sheets prepared in this same manner were annealed by holding the zinc sheet at either 140°C or 220°C for 16 hours. There was no significant difference between the cell capacities obtained by the use of either temperature. These conditions were chosen arbitrarily and probably are not optimum. The cell capacities using these annealed electrodes are plotted as lines D of Fig. 3. The slopes of the lines in Fig. 3 were determined statistically using Eq. (1).

Effect of Grain Structure of Zinc on Cell Capacity

The data in Fig. 3 shows that significant variations in capacity are obtained from zinc electrodes prepared in different ways. A portion, if not all, of this variation may be attributed to differences in the grain structure of the zinc. Annealing of the cast and rolled, pure zinc electrodes increased their capacity by 8 percent.

Unfortunately, most of the data for zinc-alloy electrodes were taken on rolled-sheet alloys before it was discovered that their capacity would have been increased by annealing.

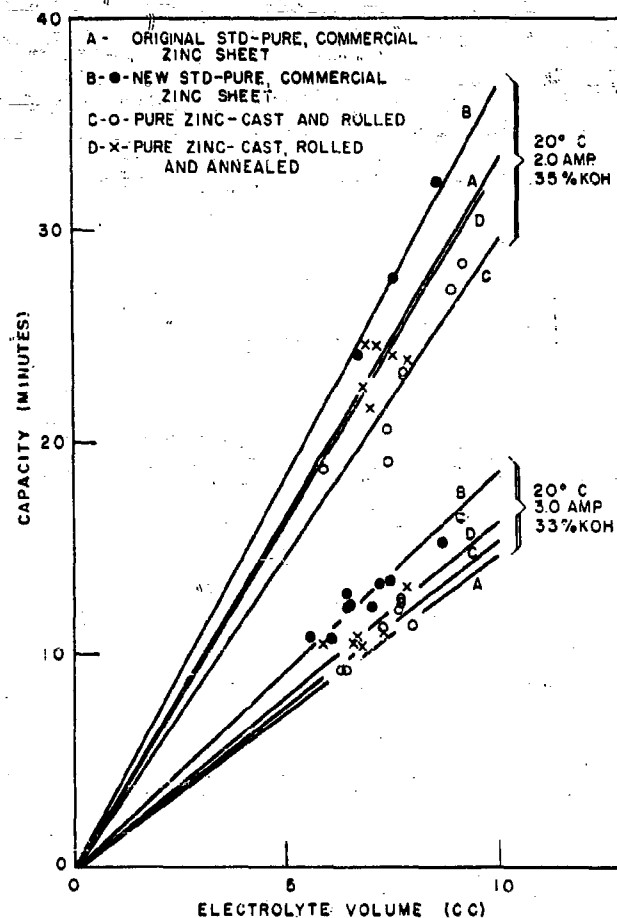


Fig. 3 - Cell capacities of pure zinc electrodes

However, a few capacities were obtained on the annealed electrodes and also on quenched electrodes. These results are shown in Table 3. The electrodes were annealed by heating the rolled-sheet alloys to 220° C for 16 hours and slowly cooling to room temperature. The quenched electrodes were prepared by heating the rolled-sheet alloys to approximately 370° C and then immersing them in cold water.

The data in Table 3 show that for a number of different alloys the rolled sheet gives an average of 20.3 percent more cell capacity than the quenched; the annealed gives 6.2 percent more than the rolled and 24.9 percent more than the quenched. These differences in cell capacity are statistically significant and are large enough to be of importance in cell design.

The conditions of annealing and quenching, to a certain extent, were arbitrarily chosen. It is quite likely that other conditions could be found which would give even greater variation in cell capacities.

The data in Table 3 were obtained at 20° C and 3.0 amperes of current. It is very probable that there are other discharge conditions which would show a much higher variation in cell capacity with change in grain structure of the electrode. This would be more likely to occur at high current densities and at low temperatures.

TABLE 3
The Effect of Quenching and Annealing on Capacity of Rolled-Sheet Zinc Electrodes Discharged at 20°C and 3.0 Amperes Using 33% KOH

Alloy	Quenched after Rolling			Rolled Sheet			Annealed after Rolling			Improvement of Rolled Over Quenched (%)	Improvement of Annealed Over Rolled (%)	Improvement of Annealed Over Quenched (%)
	Volume (cc)	Capacity (min)	Capacity (min/cc)	Volume (cc)	Capacity (min)	Capacity (min/cc)	Volume (cc)	Capacity (min)	Capacity (min/cc)			
0.050% Al	7.1	11.85	1.669	6.7	9.2	1.373	7.5	12.05	1.607	-17.7	17.0	-3.7
0.50% Al	7.45	9.9	1.329	6.7	11.1	1.657	6.6	11.5	1.742	24.7	5.1	31.1
0.51% Sb	7.85	10.0	1.274	7.0	9.9	1.414	6.85	10.4	1.518	11.0	7.4	19.2
4.73% Sb	6.75	7.4	1.096	5.9	7.7	1.305	-	-	-	19.1	-	-
0.054% Cd	-	-	-	6.5	8.3	1.277	6.8	11.2	1.647	-	29.0	-
0.050% Cu	8.6	8.65	1.006	7.4	7.9	1.068	-	-	-	6.3	-	-
0.50% Cu	-	-	-	6.8	8.9	1.309	7.5	10.4	1.387	-	6.0	-
0.050% Li	7.75	7.4	0.955	6.9	8.6	1.246	7.7	11.5	1.434	30.5	19.9	56.4
0.025% Mg	6.5	9.6	1.477	6.5	10.3	1.585	7.05	9.5	1.348	7.3	-14.9	-8.7
0.050% Mn	7.1	11.2	1.577	6.55	10.3	1.573	7.15	11.75	1.643	-0.3	4.5	4.2
0.50% Mn	7.0	10.4	1.486	6.45	12.6	1.953	7.5	13.45	1.793	31.4	-8.2	20.7
0.050% Hg	6.7	8.0	1.194	5.3	9.7	1.540	6.45	10.35	1.605	29.0	4.2	34.4
0.51% Hg	6.2	8.4	1.355	6.6	12.0	1.818	7.8	12.25	1.571	34.2	-13.6	15.9
0.99% Hg	6.8	8.7	1.279	6.3	10.9	1.730	6.6	10.9	1.652	35.2	-4.5	29.2
1.56% Hg	7.2	7.1	0.986	6.4	11.4	1.781	7.5	12.5	1.667	52.6	-6.4	69.1
0.051% Ni	6.9	8.8	1.275	6.55	7.7	1.176	6.9	11.5	1.667	-7.8	41.8	30.7
										20.3% Avg.	6.2% Avg.	24.9% Avg.

These results would also be expected to vary with different alloying elements. It can be seen that the annealing of mercury alloys causes a slight decrease in their capacity. If they were not included, the average increase in capacity obtained by annealing a rolled-sheet electrode would be 10.6 percent, which is probably a more representative value.

In the past, measurements of cell capacities obtained by the construction and discharge of individual cells have been subject to appreciable variation. Outside of mechanical and human errors, which generally are recognized readily, there appear to be two main causes of this variation. These are nicely illustrated in Fig. 3. One is the random variation of the individual data about the straight line showing the relationship of capacity to electrolyte volume, and the other is the variation in the slopes of the different straight lines. The latter variation is the result of change in the grain structure of the electrode. More work needs to be done to determine the optimum crystalline structure of zinc electrodes that would maximize cell capacity.

In view of this information the standard lines plotted in Fig. 4 are probably not the exact standards with which the individual points should be compared. However, they probably fall within several percent of the true value and are close enough for practical comparisons.

Effects of Alloying Elements on Cell Capacity

The cell capacities of the various zinc-alloy electrodes are shown in Fig. 4. These values are plotted as individual points which may be compared visually with the standards, represented as straight lines, of the expected capacity using pure zinc electrodes. There are three standards which correspond to the three sets of discharge conditions used: the topmost line is for 0.6 ampere, -20°C , 33% KOH; the second is for 2 amperes, 20°C , 35% KOH; the third, or bottom, line is for 3 amperes, 20°C , 33% KOH. Determined by the least squares method, these lines are shown in Fig. 1 and as lines A of Fig. 3.

An examination of Fig. 4 shows that the alloying elements have a widely varying effect on cell capacity. Nickel, antimony, silver, aluminum, lithium, magnesium, and copper decrease cell capacity. The decrease is generally greatest at -20°C and at the highest concentration of alloying element. Under the conditions tested, electrodes made of the alloys of lead, selenium, tellurium, strontium, thallium, sodium, arsenic, silicon, titanium, vanadium, tungsten, boron, chromium, iron, potassium, and barium showed a negligible difference in cell capacity from those made of pure zinc.

Calcium alloys showed a slight improvement at 20°C . Manganese and cobalt alloys showed improvement in capacity at 20°C and a decrease at -20°C . Cadmium showed some improvement at all conditions. Mercury showed a very definite improvement at all conditions, and in particular at -20°C where 50 percent increases in capacity were obtained.

More data are needed over a wider range of discharge conditions to confirm those results.

CONCLUSIONS

The crystalline structure of zinc and zinc-alloy electrodes has a very large effect on the capacity of the silver oxide-zinc alkaline cell. Further work needs to be done to determine the physical treatment necessary to obtain the optimum grain structure for maximizing cell capacity at various discharge conditions.

Mercury alloys of zinc give higher cell capacities than pure zinc. A few other alloying elements show some promise but need further testing.

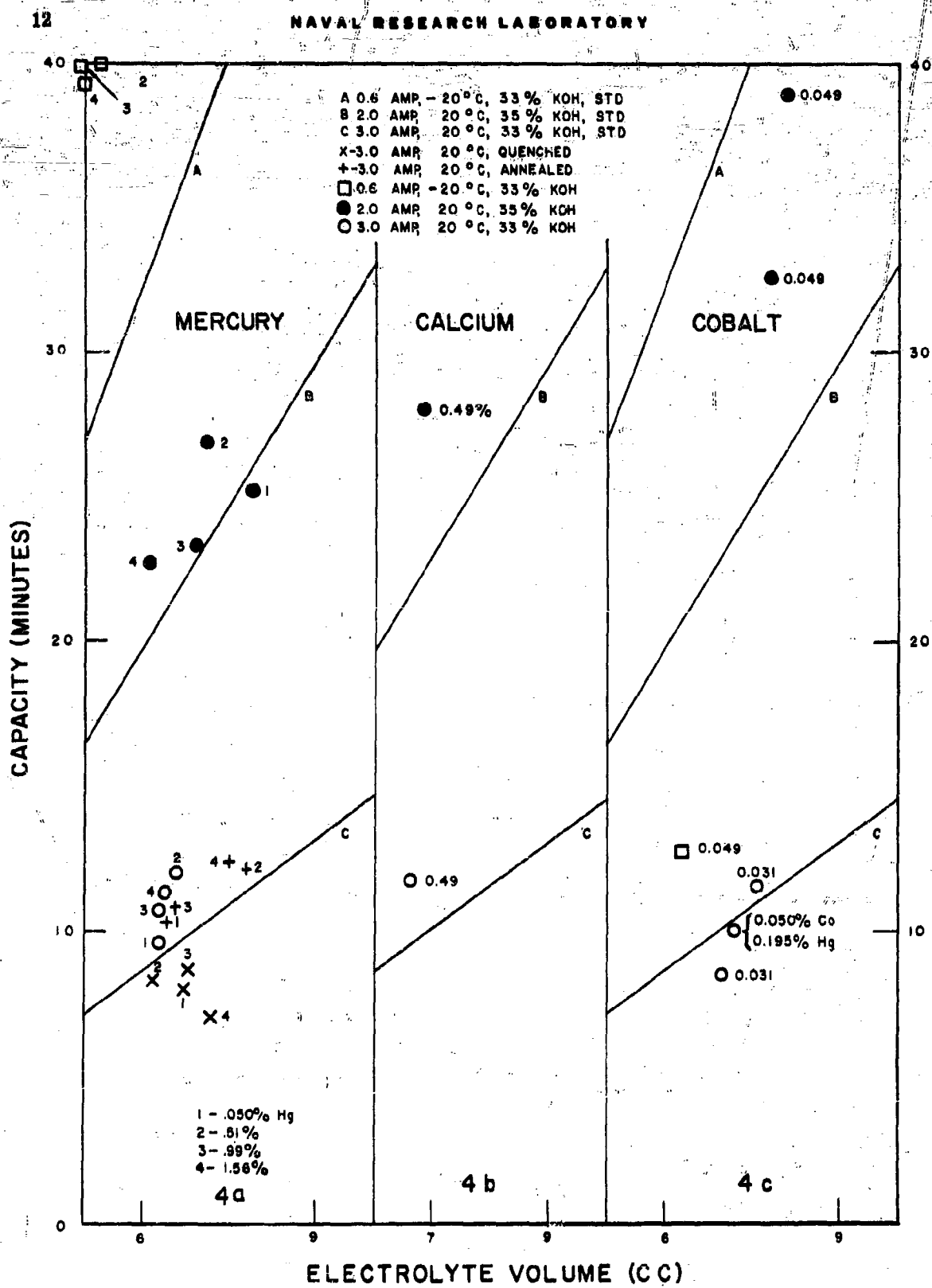


Fig. 4 - Cell capacities of zinc-alloy electrodes

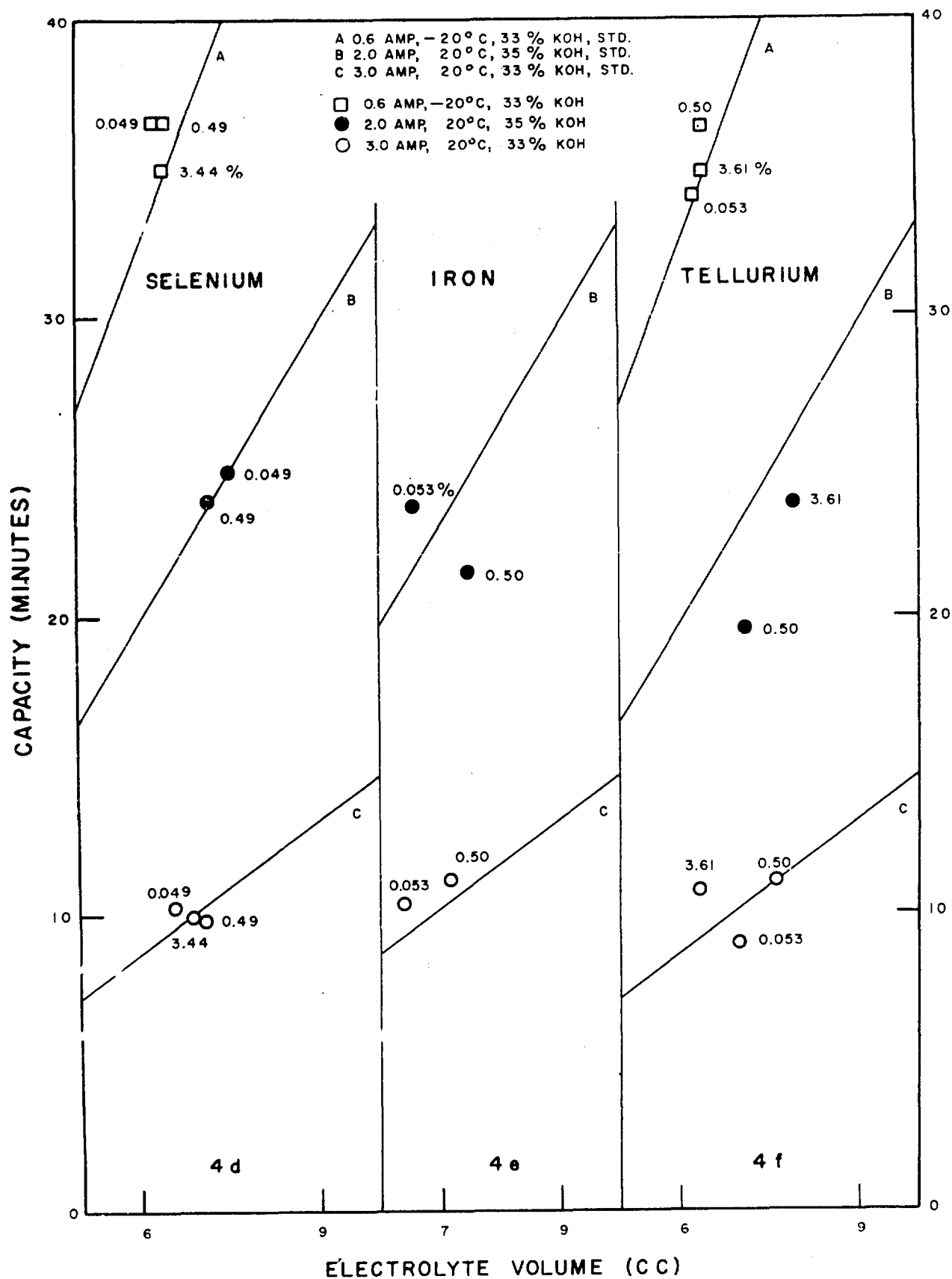


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes

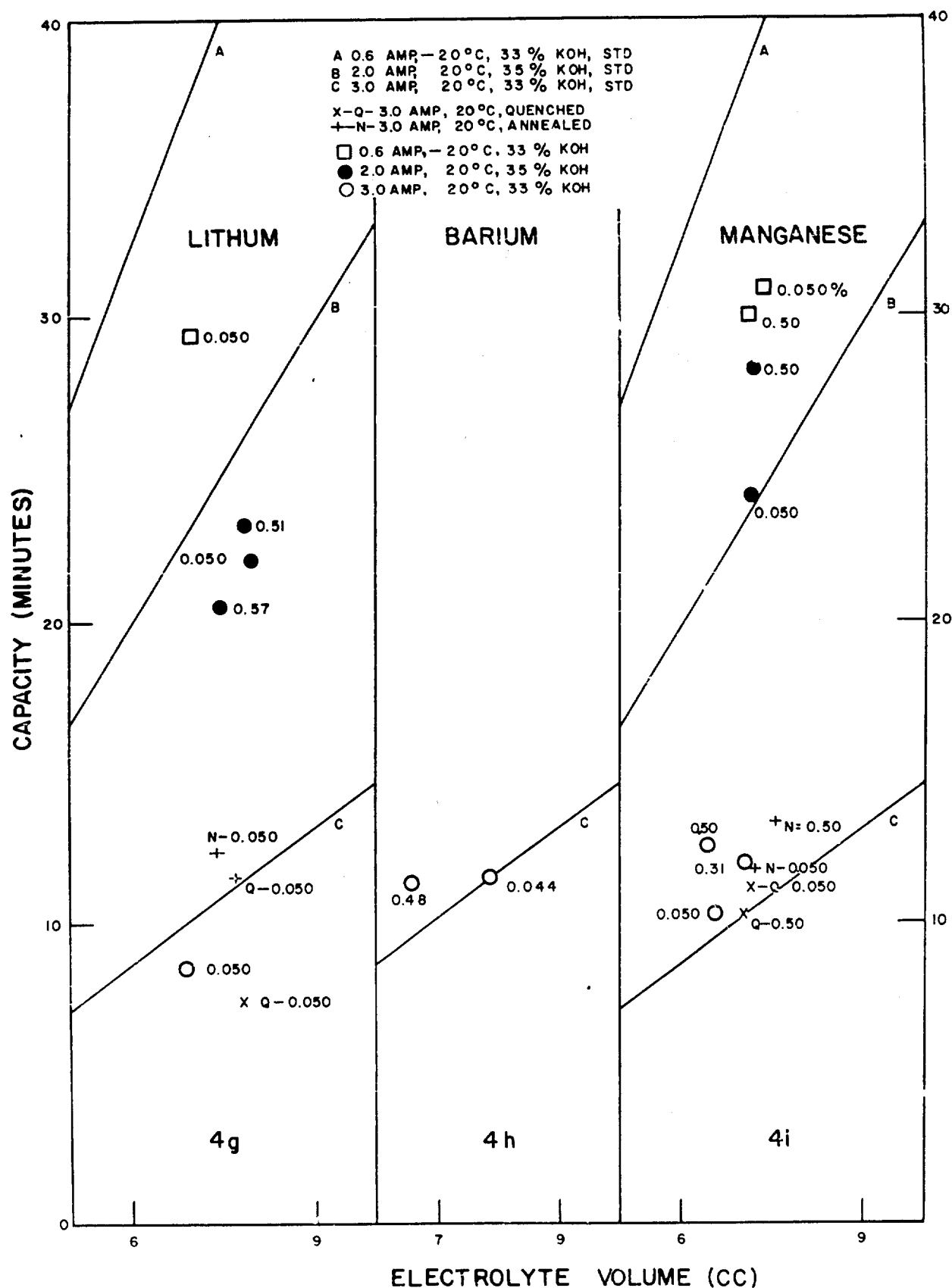


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes

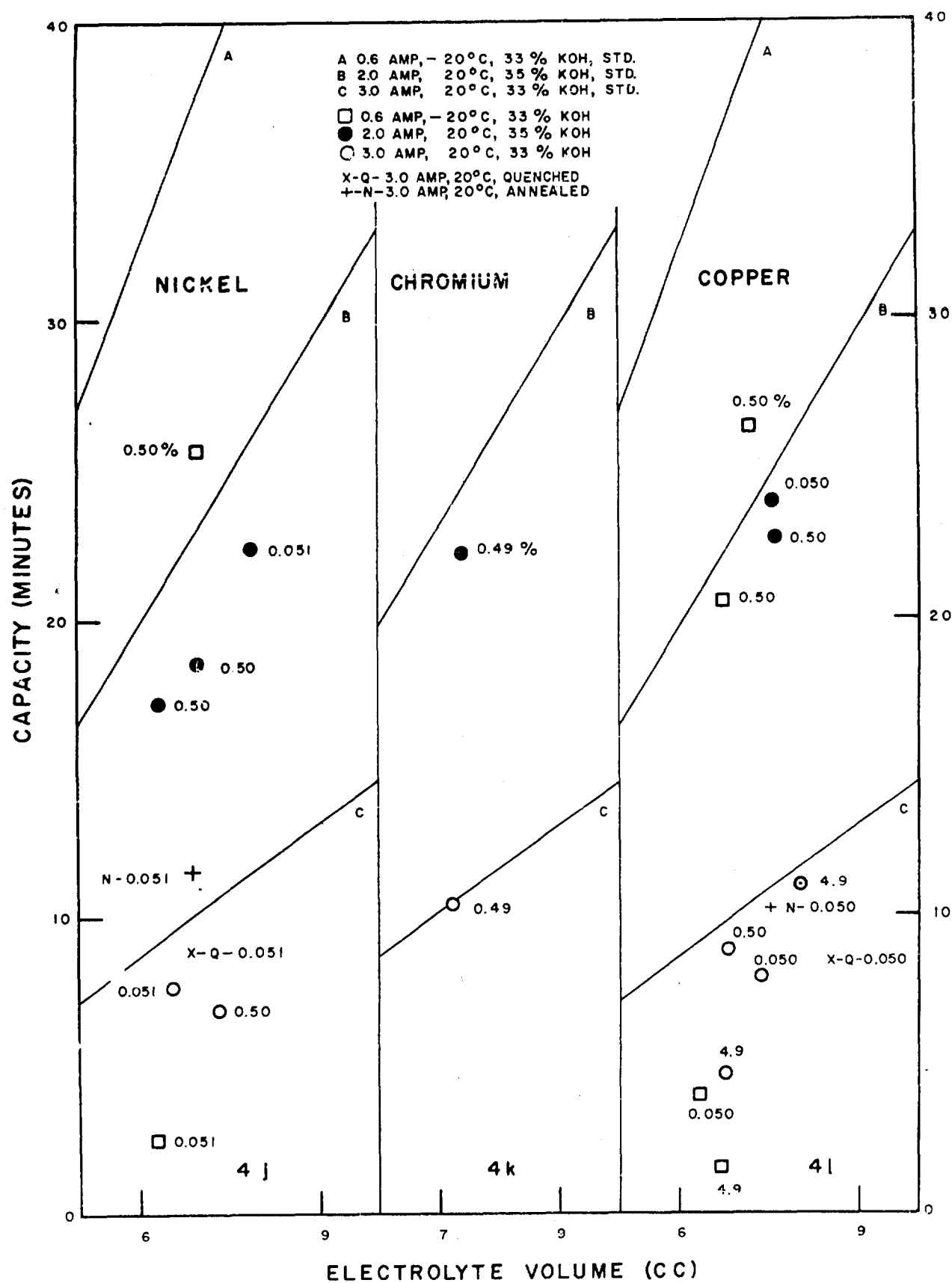


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes

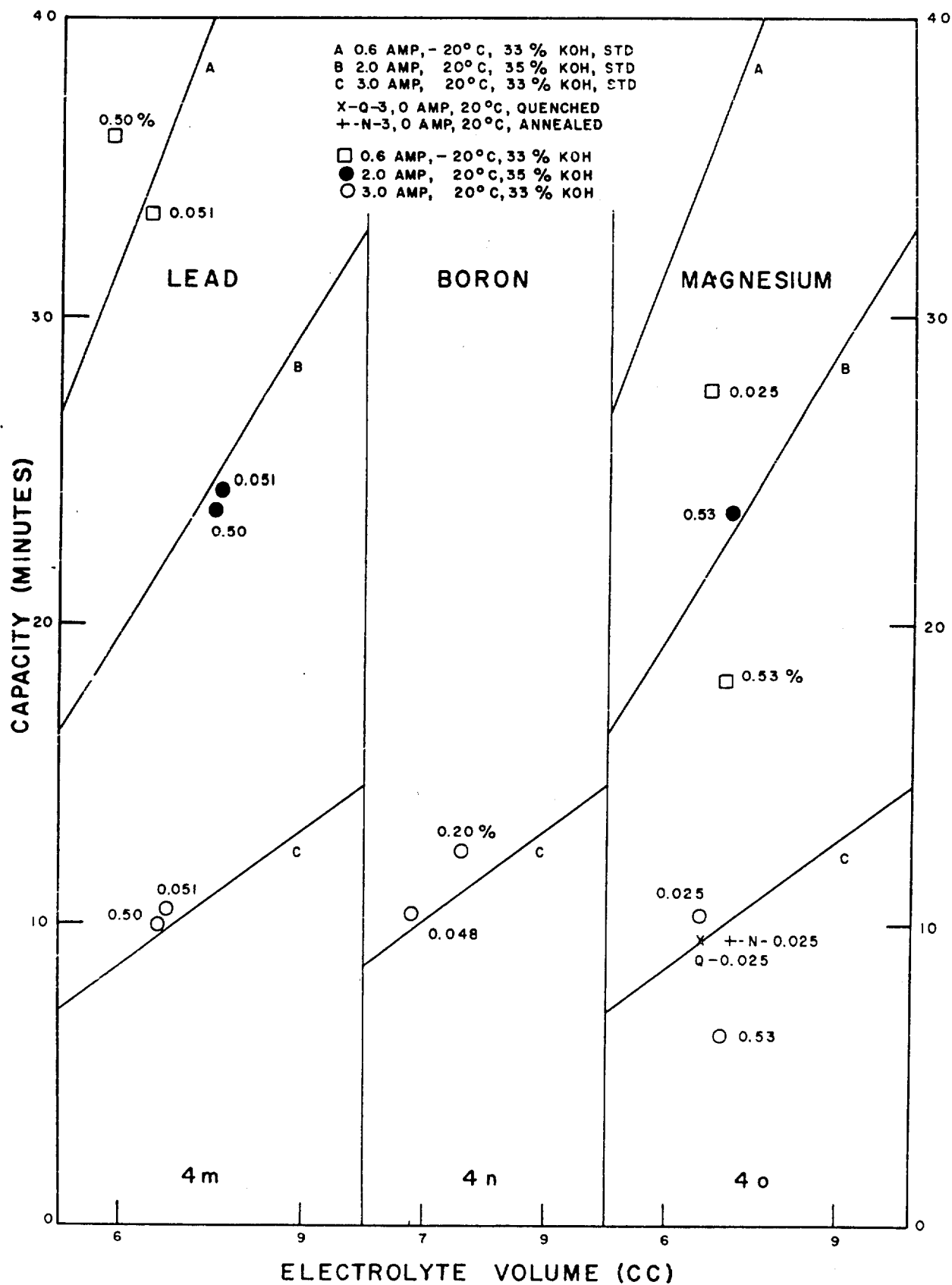


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes

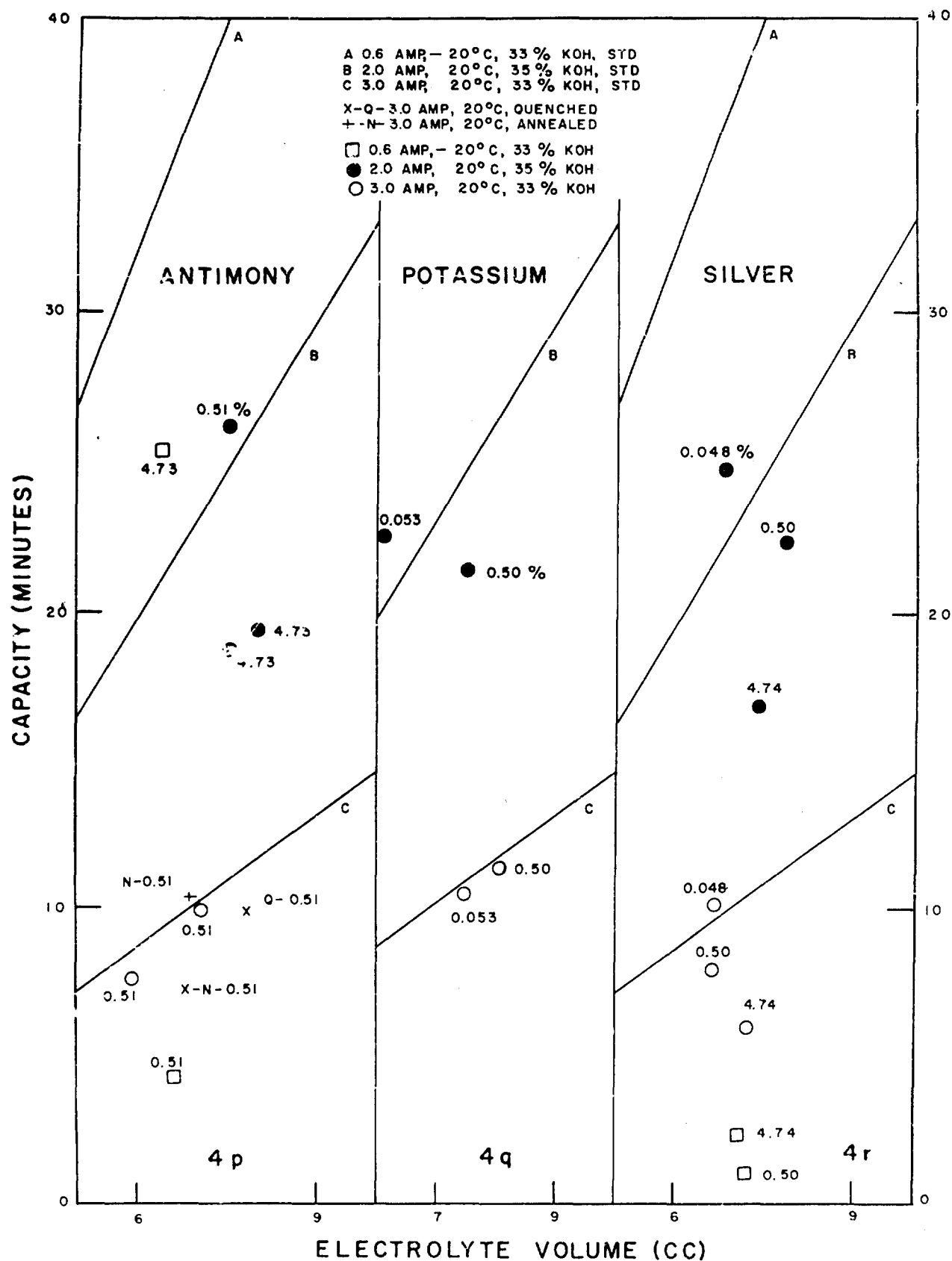


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes

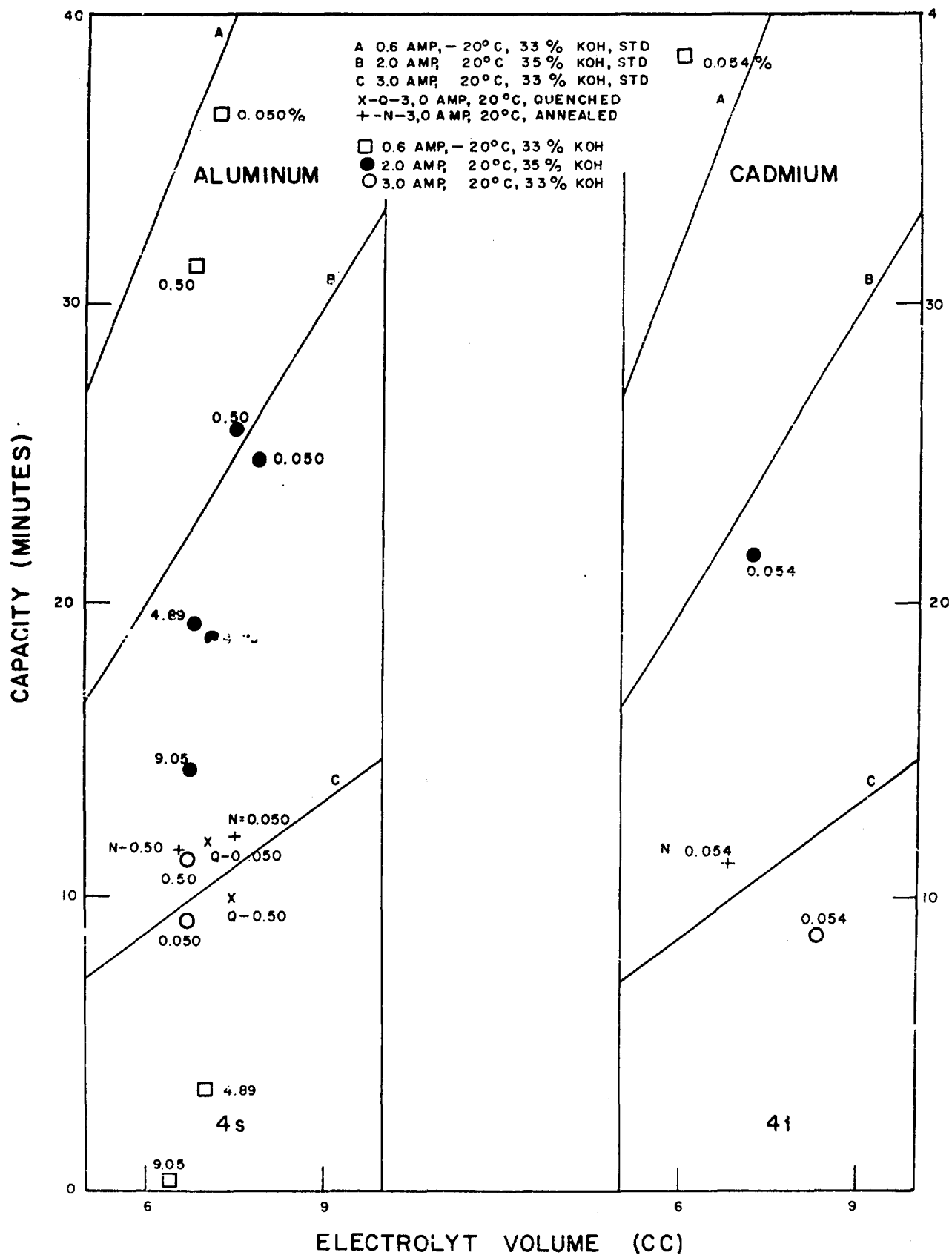


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes

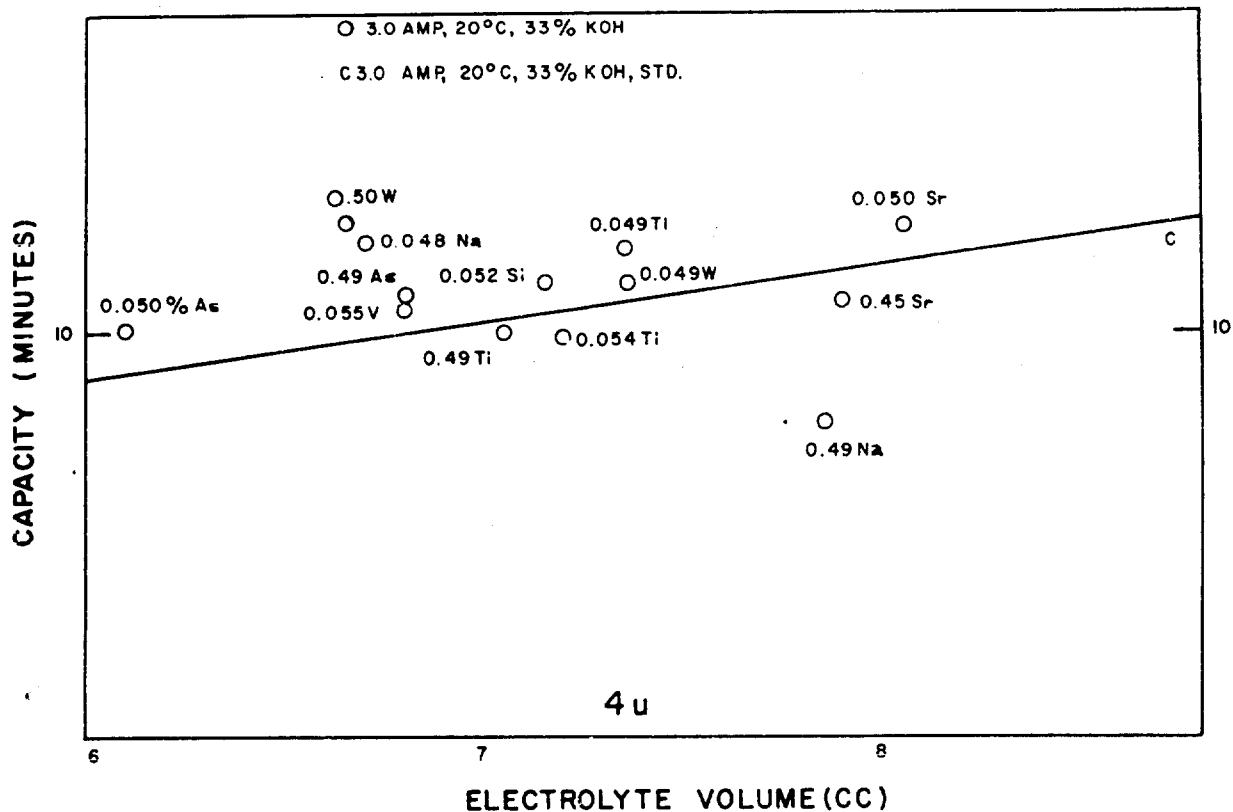


Fig. 4 (Continued) - Cell capacities of zinc-alloy electrodes. (Arsenic, sodium, silicon, strontium, titanium, thallium, vanadium, and tungsten).

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